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Self-Assembly of [3]Catenanes and a [4]Molecular Necklace Based on a Cryptand/Paraquat Recognition Motif

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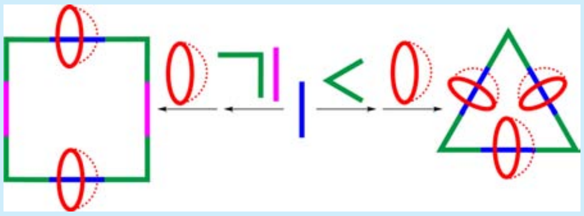
Supporting Information



ABSTRACT: Hierarchical self-assembly centered on metallacyclic scaffolds greatly facilitates the construction of mechanically interlocked structures. The formation of two [3]catenanes and one [4]molecular necklace is presented by utilizing the orthogonality of coordination-driven self-assembly and crown ether-based cryptand/paraquat derivative complexation. The threaded [3]catenanes and [4]molecular necklace were fabricated by using ten and nine total molecular components, respectively, from four and three unique species in solution, respectively. In all cases single supramolecular ensembles were obtained, attesting to the high degree of structural complexity made possible via self-assembly approaches.

Mechanically interlocked molecules (MIMs), such as catenanes and rotaxanes, have attracted a great deal of attention because of their topological importance, interesting physical properties, and potential applications in molecular machines, nanomaterials, and biomaterials.[1] Although a variety of promising template-directed methods have been developed to provide convenient routes to obtain MIMs with the aid of molecular recognition and/or host−guest chemistry based on noncovalent interactions, the highly efficient preparation of high-order MIMs from simple components is still a challenging task.[2]

The past three decades have witnessed a rapid growth in the field of coordination-driven self-assembly, resulting in the development of highly efficient synthetic methodologies for the preparation of discrete supramolecular entities. Thus, an assortment of one- (1D), two- (2D), and three-dimensional (3D) finite supramolecular coordination complexes (SCCs) with well-defined shapes and sizes have been constructed via coordination-driven self-assembly.[3] This highly efficient and versatile approach has more recently been applied toward the construction of MIMs.[4−7] The formation of MIM systems can be greatly simplified if one or more segments are generated by coordination-driven self-assembly methods.[4−7] Some MIMs, such as rotaxanes,[4] catenanes,[5] links,[6] and supramolecular polymers,[7] have been elegantly fabricated via orthogonal or hierarchical self-assembly based on coordination-driven self-assembly and host−guest chemistry.[8] Very recently, we reported the formation of a suite of catenanes and molecular necklaces, by employing the orthogonality between coordination-driven self-assembly and a well-developed recognition motif of 1,2-bis(pyridinium)ethane/dibenzo[24]crown-8.[9]

Crown ether-based cryptands usually possess much better binding affinities than the corresponding simple crown ethers on account of both the preorganization of the hosts during the association process and the introduction of additional and/or spatially optimized binding sites.[10] For example, the association constant (K_a)[10c] of the complex between bis(*m*-phenylene)-32-crown-10-based cryptand **1** (Scheme 1) and paraquat was determined to be 5.0×10^6 M^{-1} in acetone, which was 9000 times greater than that of the complex derived from bis(*m*-phenylene)-32-crown-10 (BMP32C10) and paraquat. Hence, the BMP32C10-based cryptand/paraquat recognition motif was particularly powerful as the impetus for the hierarchical self-assembly of MIMs.[11] Herein, we extended our previously reported orthogonal self-assembly strategy to the fabrication of MIMs based on the BMP32C10-based cryptand/paraquat recognition motif. Two [3]catenanes were constructed; a total of 10 molecular components from four unique building blocks were used. Similarly, a [4]molecular necklace was formed with a total of 9 molecular components from three unique building blocks.

As shown in Scheme 1, by stirring a paraquat-derived carboxylate ligand (**2**), *cis*-$Pt(PEt_3)_2(OTf)_2$ (**3**), and dipyridyl ligand **4** (**4a** or **4b**) with a 1:2:1 ratio first in H_2O/acetone and then in acetone-d_6, guest-containing rectangles, **5** (**5a** or **5b**), were obtained in one pot via multicomponent heteroligated self-assembly. Multinuclear NMR (^{31}P and ^1H) spectroscopy of the reaction solution supported the formation of single, discrete metallacycles with highly symmetric structures. The $^{31}P\{^1H\}$ NMR spectra of **5** (**5a** or **5b**) displayed two coupled doublets of approximately equal intensity with concomitant ^{195}Pt satellites, which was consistent with the multicomponent Pt−N,O

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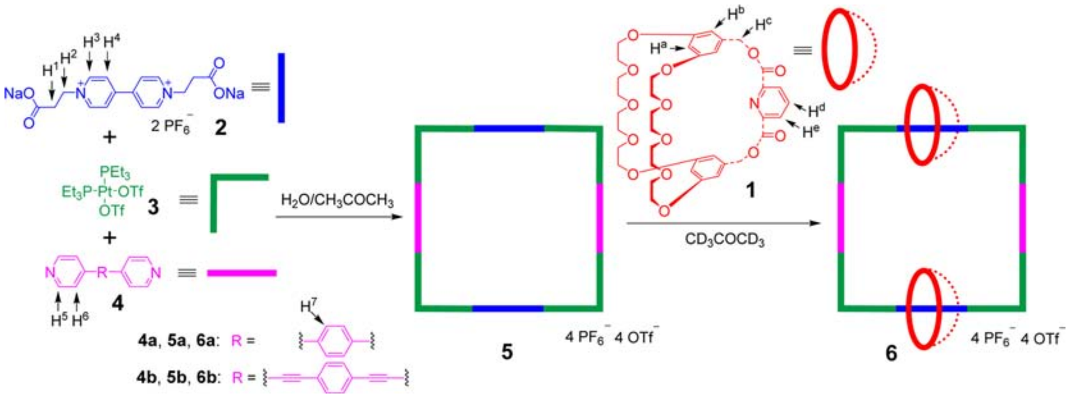
Scheme 1. Self-Assembly of Supramolecular Rectangles and [3]Catenanes



heterolligated coordination environment wherein each Pt(II) center of **5** (**5a** or **5b**) coordinated with one pyridyl and one carboxylate moiety (Figures S1−S4). Following the formation of the rectangular metallacycles **5** (**5a** or **5b**), BMP32C10-based cryptand **1** was added to the solutions *in situ* and the mixtures were stirred overnight at room temperature to allow the generation of [3]catenane **6** (**6a** or **6b**). After the addition of **1**, the color of the solutions changed from colorless to bright yellow, suggesting the presence of intermolecular charge transfer between the host and guest.

The threading of rectangle **5a** with **1** was characterized by ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. Upon the addition of 1.0 equiv of **1** to a 1.0 mM solution of **5a**, two new sets of peaks appeared in the ^{31}P{^{1}H} NMR spectrum (Figure 1b), corresponding to the formation of [3]catenane **6a**. When 3.0 equiv of **1** were added, almost all of the free metallacycles were threaded to deliver **6a** (Figure 1c). This trend was also observed in a ^{1}H NMR titration experiment (Figure 2). After 3.0 equiv of **1** were added, the ^{1}H NMR spectrum showed two sets of resonances for uncomplexed **1** and [3]catenane **6a**. The simultaneous observation of peaks associated with both species supports a slow exchange between threaded and unthreaded forms on the ^{31}P{^{1}H} and ^{1}H NMR time scales at room temperature, in stark contrast to the fast exchange between cryptand **1** and paraquat.[10] The peaks for aromatic protons H^{a}, H^{b} and methylene protons H^{c} of **1** and pyridinium protons H^{3} of **5a** shifted upfield upon formation of [3]catenane **6a**, while those of the pyridinyl protons H^{d} and H^{e} of **1**, and H^{1}, H^{2}, H^{4}, H^{5}, H^{6}, and H^{7} on **5a** moved downfield. The threading process of [3]catenane **6b** resulted in similar ^{31}P{^{1}H} and ^{1}H NMR spectra (Figures S11 and S12).

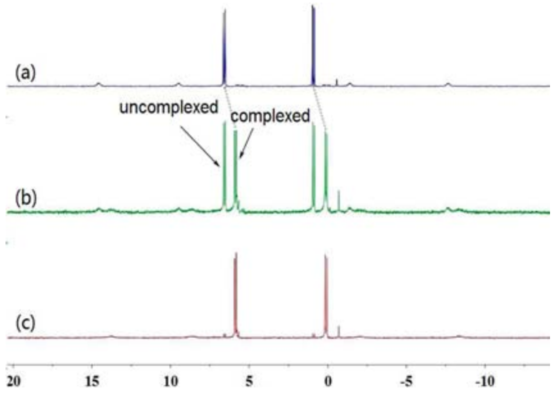


Figure 1. Partial ^{31}P{^{1}H} NMR (202.3 MHz, acetone-d_6, 22 °C) spectra of (a) metallacycle **5a** (1.0 mM), (b) **5a** (1.0 mM) + **1** (1.0 mM), and (c) **5a** (1.0 mM) + **1** (3.0 mM).

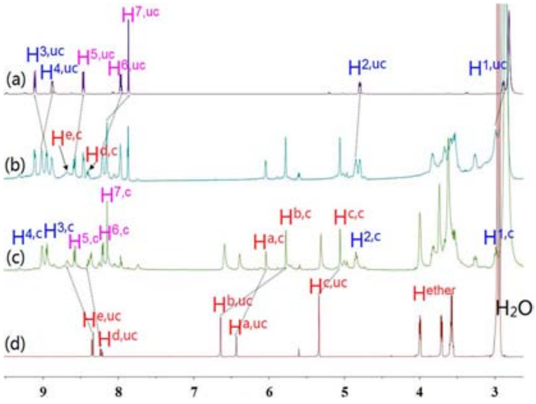
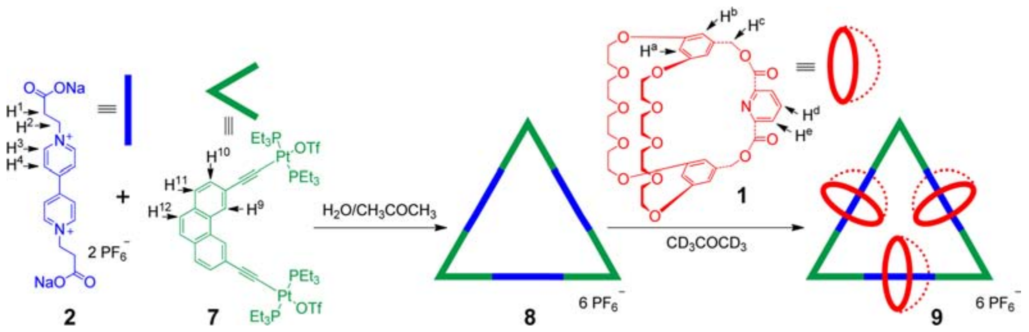


Figure 2. Partial ^{1}H NMR (500 MHz, acetone-d_6, 22 °C) spectra of (a) metallacycle **5a** (1.0 mM), (b) **5a** (1.0 mM) + **1** (1.0 mM), (c) **5a** (1.0 mM) + **1** (3.0 mM), and (d) **1**. Complexed and uncomplexed species are denoted by "c" and "uc", respectively.

The hierarchical self-assembly of the triangular [4]molecular necklace **9** was induced using a similar strategy to that of **6a** and **6b** (Scheme 2). An initial self-assembly between **2** and a 60° Pt(II) acceptor (**7**) furnished discrete metallacycle **8**. Multinuclear NMR (^{31}P and ^{1}H) analysis of the reaction solution supported the formation of the highly symmetric triangle **8** (Figures S5 and S6). The ^{31}P{^{1}H} NMR spectrum of **8** exhibited a singlet at 18.83 ppm, which was accompanied by ^{195}Pt satellites (Figure S5). The addition of **1** to a solution of **8** in acetone resulted in the generation of [4]molecular necklace **9** after stirring overnight at room temperature. A color change from pale to bright yellow was also observed upon the introduction of **1**. The threading process between **8** and **1** was monitored by ^{31}P{^{1}H} (Figure 3) and ^{1}H NMR (Figure 4) spectroscopy. When **1** was added to a solution of **8** in acetone-d_6, new sets of peaks appeared in both the ^{31}P{^{1}H} NMR (Figure 3b) and ^{1}H NMR spectra (Figure 4b), indicative of the formation of **9**. After 3.3 equiv of **1** were added, almost all of **8** became threaded (Figure 3b and Figure 4b), indicating that a significant excess of host was not required for threading the trigonal system. This efficacy implied a high binding constant for the complexation between **1** and paraquat derivatives. Upon the formation of **9**, the proton signals for H^{a}, H^{b}, and H^{c} of **1** and protons H^{1}, H^{2}, H^{3}, and H^{4} of **2** shifted upfield, while those for protons H^{9}, H^{10}, H^{11}, and H^{12} on **7** and the pyridinium protons H^{d} and H^{e} on **1** only displayed

Scheme 2. Self-Assembly of Supramolecular Triangle and [4]Molecular Necklace



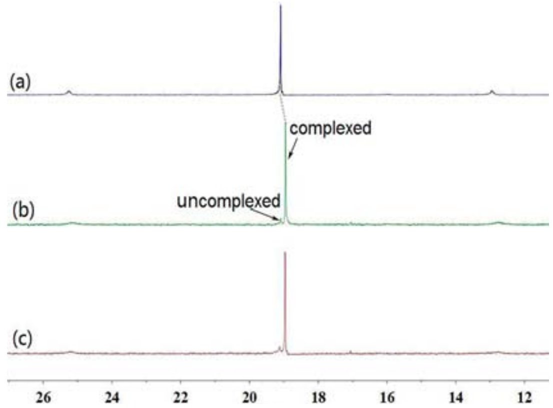


Figure 3. $^{31}P\{^1H\}$ NMR (202.3 MHz, acetone-d_6, 22 °C) spectra of (a) metallacycle **8** (1.0 mM), (b) **8** (1.0 mM) + **1** (3.3 mM), and (c) **8** (1.0 mM) + **1** (6.6 mM).

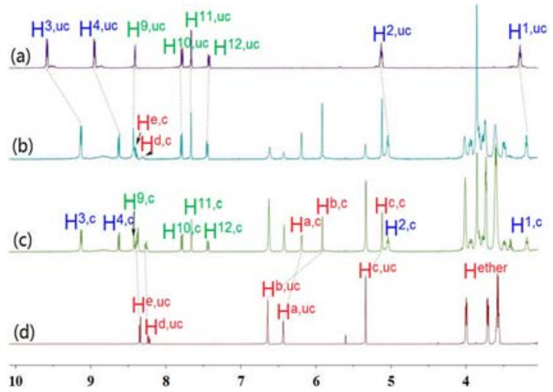


Figure 4. Partial ^1H NMR (500 MHz, acetone-d_6, 22 °C) spectra of (a) metallacycle **8** (1.0 mM), (b) **8** (1.0 mM) + **1** (3.3 mM), (c) **8** (1.0 mM) + **1** (6.6 mM), and (d) **1**. Complexed and uncomplexed species are denoted by "c" and "uc", respectively.

small changes. After 6.6 equiv of **1** were added, the ^1H NMR spectrum became sharper and clearer (Figure 4c), suggesting the formation of a single, thermodynamically stable supramolecular structure.

The host–guest interactions occurring in [3]catenanes **6** and [4]molecular necklace **9** were further confirmed by 2D NOESY NMR experiments. In the NOESY NMR spectrum of a mixture of **5a** and **1**, NOE was observed between ether protons H^{ether} on **1** and ethane protons $H^{2,c}$ on **2** (Figure S15). Likewise, NOE existed between $H^{b,c}$ on **1** and ethane protons $H^{1,c}$ on **2** in the NOESY NMR spectrum of a mixture of **5b** and **1** (Figure S16). NOE was also found between ether protons H^{ether} on **1** and pyridinium protons $H^{3,c}$ on **2** in the NOESY NMR spectrum of a mixture of **8** and **1** (Figure S17).

Electrospray ionization mass spectrometry (ESI-MS) studies provided further evidence for the stoichiometry of formation of the assembled metallacycles, catenanes, and molecular necklace. In the ESI mass spectrum of **6a**, two related peaks that supported the [3]catenane **6a** structural assignment were observed (Figure S21), including a peak at m/z = 1661.11, attributed to [**6a** − 3HOTf + 1Na + $1NH_4$ + 1H]$^{3+}$ (Figure 5). In the ESI mass spectrum of **6b**, two peaks (Figure S22) relevant to the intact self-assembly were observed. With respect to **9**, two peaks (Figure S23), including a peak at m/z = 1613.76 belonging to [**9** − $6HPF_6$ + 2K + 1Na + $1NH_4$]$^{4+}$ (Figure 5), were found, which supported the formation of a [4]molecular necklace structure. Ten and four relevant peaks were observed for metallacycle **5a** and **5b** (Figures S18 and S19), respectively, while six peaks were found that supported the assignment of triangle **8** (Figure S20). All of these peaks were isotopically resolved and agreed very well with their calculated theoretical distributions.

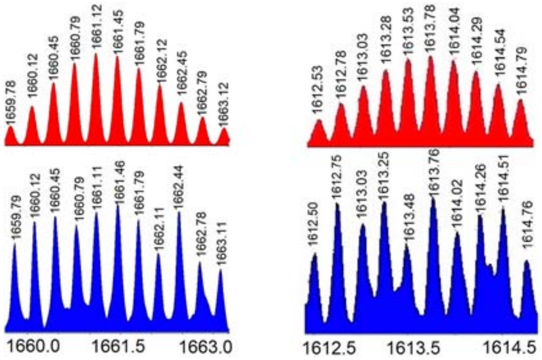


Figure 5. ESI-MS spectra of [**6a** − 3HOTf + 1Na + $1NH_4$ + 1H]$^{3+}$ (left, bottom, blue) and [**9** − $6HPF_6$ + 2K + 1Na + $1NH_4$]$^{4+}$ (right, bottom, blue), and their simulated spectra (top, red).

In conclusion, two [3]catenanes and one [4]molecular necklace were efficiently constructed via hierarchical assembly that used both coordination-driven self-assembly and the host–guest recognition between BMP32C10-based cryptand **1** and paraquat-derived carboxylate ligand **2** as complementary methods. Studies on the dynamics of threading and the structures of the resulting [3]catenanes and [4]molecular necklace were conducted using ^1H NMR, ^{31}P NMR, 2D NOESY NMR, and ESI-MS. This orthogonal design strategy, which successively uses highly efficient coordination-driven self-assembly and the host–guest complexation with favorable binding constants, greatly facilitates the construction of MIMs with high structural complexity from simple components. This method is readily adapted to the self-assembly of other topologically complex supermolecules.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures and characterization data for all self-assemblies. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01211.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72. (b) Niu, Z.; Gibson, H. W. *Chem. Rev.* **2009**, *109*, 6024. (c) Forgan, R. S.; Sauvage, J.-P.; Stoddart, J. F. *Chem. Rev.* **2011**, *111*, 5434. (d) Durola, F.; Heitz, V.; Reviriego, F.; Roche, C.; Sauvage, J.-P.; Sour, A.; Trolez, Y. *Acc. Chem. Res.* **2014**, *47*, 633. (e) Bruns, C. J.; Stoddart, J. F. *Acc. Chem. Res.* **2014**, *47*, 2186. (f) Langton, M. J.; Beer, P. D. *Acc. Chem. Res.* **2014**, *47*, 1935.

(2) (a) Fang, L.; Basu, S.; Sue, C.-H.; Fahrenbach, A. C.; Stoddart, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 396. (b) Zhang, Z.-J.; Zhang, H.-Y.; Wang, H.; Liu, Y. *Angew. Chem., Int. Ed.* **2011**, *50*, 10834. (c) Zhu, K.; Vukotic, V. N.; Loeb, S. J. *Angew. Chem., Int. Ed.* **2012**, *51*, 2168. (d) Frasconi, M.; Kikuchi, T.; Cao, D.; Wu, Y.; Dyar, S. M.; Liu, W.-G.; Barin, G.; Sarjeant, A. A.; Carmieli, R.; Wang, C.; Wasielewski, M. R.; Goddard, W. A., III; Stoddart, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 11011. (e) Ayme, J.-F.; Gil-Ramírez, G.; Leigh, D. A.; Lemonnier, J.-F.; Markevicius, A.; Muryn, C. A.; Zhang, G. *J. Am. Chem. Soc.* **2014**, *136*, 13142.

(3) (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853. (b) Fujita, M.; Tominaga, M.; Hori, A.; Therrien, B. *Acc. Chem. Res.* **2005**, *38*, 371. (c) Yoshizawa, M.; Klosterman, J. K.; Fujita, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 3418. (d) Chakrabarty, R.; Mukherjee, P. S.; Stang, P. J. *Chem. Rev.* **2011**, *111*, 6810. (e) Cook, T. R.; Zheng, Y.-R.; Stang, P. J. *Chem. Rev.* **2013**, *113*, 734. (f) Smulders, M. M. J.; Riddell, I. A.; Browne, C.; Nitschke, J. R. *Chem. Soc. Rev.* **2013**, *42*, 1728. (g) Yan, X.; Li, S.; Pollock, B. J.; Cook, T. R.; Chen, J.; Zhang, Y.; Ji, X.; Yu, Y.; Huang, F.; Stang, P. J. *Proc. Natl. Acad. Sci. U.S.A.* **2013**, *110*, 15585. (h) Wei, P.; Cook, T. R.; Yan, X.; Huang, F.; Stang, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 15497. (i) Zhou, F.; Li, S.; Cook, T. R.; He, Z.; Stang, P. J. *Organometallics* **2014**, *33*, 7019. (j) Sun, B.; Wang, M.; Lou, Z.; Huang, M.; Xu, C.; Li, X.; Chen, L.-J.; Yu, Y.; Davis, G. L.; Xu, B.; Yang, H.-B.; Li, X. *J. Am. Chem. Soc.* **2015**, *137*, 1556. (k) Lu, X.; Li, X.; Guo, K.; Xie, T.-Z.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *J. Am. Chem. Soc.* **2014**, *136*, 18149. (l) Lu, X.; Li, X.; Guo, K.; Wang, J.; Huang, M.; Wang, J.-L.; Xie, T.-Z.; Moorefield, C. N.; Cheng, S. D.; Wesdemiotis, C.; Newkome, G. R. *Chem.—Eur. J.* **2014**, *20*, 13094. (m) Sarkar, R.; Guo, K.; Moorefield, C. N.; Saunders, M. J.; Wesdemiotis, C.; Newkome, G. R. *Angew. Chem., Int. Ed.* **2014**, *53*, 12182. (n) Ludlow, J. M., III; Xie, T.; Guo, Z.; Guo, K.; Saunders, M. J.; Moorefield, C. N.; Wesdemiotis, C.; Newkome, G. R. *Chem. Commun.* **2015**, *51*, 3820. (o) Li, Y.; Jiang, Z.; Yuan, J.; Liu, D.; Wu, T.; Moorefield, C. N.; Newkome, G. R.; Wang, P. *Chem. Commun.* **2015**, *51*, 5766.

(4) (a) Jeong, K. S.; Choi, J. S.; Chang, S. Y.; Chang, H. Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 1692. (b) Hunter, C. A.; Low, C. M. R.; Packer, M. J.; Spey, S. E.; Vinter, J. G.; Vysotsky, M. O.; Zonta, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2678. (c) Chang, S.-Y.; Jeong, K.-S. *J. Org. Chem.* **2003**, *68*, 4014.

(5) (a) Fujita, M.; Fujita, N.; Ogura, K.; Yamaguchi, K. *Nature* **1999**, *400*, 52. (b) Yamauchi, Y.; Yoshizawa, M.; Fujita, M. *J. Am. Chem. Soc.* **2008**, *130*, 5832. (c) Blanco, V.; Chas, M.; Abella, D.; Peinador, C.; Quintela, J. M. *J. Am. Chem. Soc.* **2007**, *129*, 13978. (d) Liu, Y.; Bruneau, A.; He, J.; Abliz, Z. *Org. Lett.* **2008**, *10*, 765. (e) Forgan, R. S.; Friedman, D. C.; Stern, C. L.; Bruns, C. J.; Stoddart, J. F. *Chem. Commun.* **2010**, *46*, 5861. (f) Blanco, V.; Garcia, M. D.; Peinador, C.; Quintela, J. M. *Chem. Sci.* **2011**, *2*, 2407. (g) Wu, J.; Fang, F.; Lu, W. Y.; Hou, J. L.; Li, C.; Wu, Z. Q.; Jiang, X. K.; Li, Z. T.; Yu, Y. H. *J. Org. Chem.* **2011**, *76*, 4682. (h) Freye, S.; Hey, J.; Galan, A. T.; Stalke, D.; Irmer, R. H.; John, M.; Clever, G. H. *Angew. Chem., Int. Ed.* **2012**, *51*, 2191. (i) Black, S. P.; Stefankiewicz, A. R.; Smulders, M. M. J.; Sattler, D.; Schalley, C. A.; Nitschke, J. R.; Sanders, J. K. M. *Angew. Chem., Int. Ed.* **2013**, *52*, 5749.

(6) Peinador, C.; Blanco, V.; Quintela, J. M. *J. Am. Chem. Soc.* **2009**, *131*, 920.

(7) (a) Wang, F.; Zhang, J.; Ding, X.; Dong, S.; Liu, M.; Zheng, B.; Li, S.; Wu, L.; Yu, Y.; Gibson, H. W.; Huang, F. *Angew. Chem., Int. Ed.* **2010**, *49*, 1090. (b) Yan, X.; Cook, T. R.; Pollock, B. J.; Wei, P.; Zhang, Y.; Yu, Y.; Huang, F.; Stang, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 4460. (c) Li, Z.-Y.; Zhang, Y.; Zhang, C.-W.; Chen, L.-J.; Wang, C.; Tan, H.; Yu, Y.; Li, X.; Yang, H.-B. *J. Am. Chem. Soc.* **2014**, *136*, 8577. (d) Tian, Y.-K.; Shi, Y.-G.; Yang, Z.-S.; Wang, F. *Angew. Chem., Int. Ed.* **2014**, *53*, 6090. (e) Tian, Y.-K.; Yang, Z.-S.; Lv, X.-Q.; Yao, R.-S.; Wang, F. *Chem. Commun.* **2014**, *50*, 9477. (f) Wei, P.; Xia, B.; Zhang, Y.; Yu, Y.; Yan, X. *Chem. Commun.* **2014**, *50*, 3973. (g) Wei, P.; Li, S.; Zhang, Y.; Yu, Y.; Yan, X. *Polym. Chem.* **2014**, *5*, 3972. (h) Wei, P.; Li, J.; Yan, X.; Zhou, Q. *Org. Lett.* **2014**, *16*, 126.

(8) (a) Yang, H.-B.; Ghosh, K.; Northrop, B. H.; Zheng, Y.-R.; Lyndon, M. M.; Muddiman, D. C.; Stang, P. J. *J. Am. Chem. Soc.* **2007**, *129*, 14187. (b) Zhu, K.; He, J.; Li, S.; Liu, M.; Feng, W.; Zhang, M.; Abliz, Z.; Huang, F. *J. Org. Chem.* **2009**, *74*, 3905. (c) Saha, M. L.; De, S.; Pramanik, S.; Schmittel, M. *Chem. Soc. Rev.* **2013**, *42*, 6860. (d) Wei, P.; Yan, X.; Huang, F. *Chem. Soc. Rev.* **2015**, *44*, 815.

(9) (a) Li, S.; Huang, J.; Cook, T. R.; Pollock, B. J.; Kim, H.; Chi, K.-W.; Stang, P. J. *J. Am. Chem. Soc.* **2013**, *135*, 2084. (b) Li, S.; Huang, J.; Zhou, F.; Cook, T. R.; Yan, X.; Ye, Y.; Zhu, B.; Zheng, B.; Stang, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 5908.

(10) (a) Bryant, W. S.; Jones, J. W.; Mason, P. E.; Guzei, I. A.; Rheingold, A. L.; Nagvekar, D. S.; Gibson, H. W. *Org. Lett.* **1999**, *1*, 1001. (b) Huang, F.; Fronczek, F. R.; Gibson, H. W. *J. Am. Chem. Soc.* **2003**, *125*, 9272. (c) Huang, F.; Switek, K. A.; Zakharov, L. N.; Fronczek, F. R.; Slebodnick, C.; Lam, M.; Golen, J. A.; Bryant, W. S.; Mason, P. E.; Rheingold, A. L.; Ashraf-Khorassani, M.; Gibson, H. W. *J. Org. Chem.* **2005**, *70*, 3231. (d) Gibson, H. W.; Wang, H.; Slebodnick, C.; Merola, J.; Kassel, W. S.; Rheingold, A. L. *J. Org. Chem.* **2007**, *72*, 3381. (e) Pederson, A. M.-P.; Ward, E. M.; Schoonover, D. V.; Slebodnick, C.; Gibson, H. W. *J. Org. Chem.* **2008**, *73*, 9094. (f) Zhang, M.; Zhu, K.; Huang, F. *Chem. Commun.* **2010**, *46*, 8131. (g) Zhang, M.; Yan, X.; Huang, F.; Niu, Z.; Gibson, H. W. *Acc. Chem. Res.* **2014**, *47*, 1995.

(11) (a) Li, S.; Liu, M.; Zhang, J.; Zheng, B.; Zhang, C.; Wen, X.; Li, N.; Huang, F. *Org. Biomol. Chem.* **2008**, *6*, 2103. (b) Li, S.; Liu, M.; Zhang, J.; Zheng, B.; Wen, X.; Li, N.; Huang, F. *Eur. J. Org. Chem.* **2008**, 6128. (c) Li, S.; Liu, M.; Zheng, B.; Zhu, K.; Wang, F.; Li, N.; Zhao, X.-L.; Huang, F. *Org. Lett.* **2009**, *11*, 3350. (d) Wang, F.; Zhou, Q.; Zhu, K.; Li, S.; Wang, C.; Liu, M.; Li, N.; Fronczek, F. R.; Huang, F. *Tetrahedron* **2009**, *65*, 1488. (e) Liu, M.; Li, S.; Hu, M.; Wang, F.; Huang, F. *Org. Lett.* **2010**, *12*, 760.